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Preparation and luminescence performance of rare earth agriculture-used light transformation composites

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Abstract Rare earth elements (REEs) and their composites could promote the growth of agricultural products, which, hence, have been widely used in farms as an important trace fertilizer, especially in China. In this work, two kinds of rare earth organic complex europium-salicylic acid-[1,10-phenanthroline] (Eu(Sal)$_3$Phen) and praseodymium-salicylic acid-[1,10-phenanthroline] (Pr(Sal)$_3$Phen) were synthesized first. Then we prepared the Eu,Pr(Sal)$_3$Phen/LLDPE composites by adding Eu(Sal)$_3$Phen and Pr(Sal)$_3$Phen (with a weight ratio of Eu(Sal)$_3$Phen: Pr(Sal)$_3$Phen = 1:1) into the linear low-density polyethylene (LLDPE) matrix by mechanical mixing. The experiments of fluorescent properties showed that the composites can absorb ultraviolet light (UV) (wavelength range of 200–400 nm) and can emit red-orange light (wavelength range of 600–680 nm), which is necessary light source for growth crop. The fluorescent properties of Eu,Pr(Sal)$_3$Phen treated for different time at 160 °C and treated for 10 min at different temperatures have been tested. It has been found that the fluorescent intensity of the Eu,Pr(Sal)$_3$Phen reduced with the increase of treated time and treated temperature. Furthermore, the fluorescent properties of Eu,Pr(Sal)$_3$Phen/LLDPE composites placed at room temperature for different time have been analyzed. It has been proved that the decrease in the fluorescent intensity of the Eu,Pr(Sal)$_3$Phen/LLDPE composites is not evident within 3 months. Therefore, these composites meet the requirements of growth crop in one quarter, sufficiently.

Introduction

With the development of agricultural applications, rare earth elements (REEs) are increasingly moving into the ecosystem. REEs fertilizer is widely applied in Chinese agriculture to improve the yield and the quality of crops including tea [1, 2], tobacco [3], maize [4] etc. It has been proved in many experiments [5–7]. The key issue is transforming solar light from one (useless, for example UV light of 200–400 nm) to other (useful, for example red–orange light of 580–600 nm). As we know, the solar light contains a series of lights with different wavelengths, among which the red–orange light is the necessary source for crop growth; it can be captured by crops and converted to chemical form energy [8]. Some attempts [9–13] have been made to convert UV light into red–orange light. Salicylic acid has very strong capability of absorbing UV light. Derivatives of salicylic acid fight against drought function and the salicylic acid is prone to form stable complexes with rare earth metal [14]. Rare earth carboxylic acid complexes possess good light transformation function [15, 16]. Rare earth ion europium and praseodymium can emit red light and blue light, respectively [17–20]. In order to, this article presents the methods of synthesizing the rare earth ternary Eu(Sal)$_3$Phen and Pr(Sal)$_3$Phen and preparing the Eu,Pr(Sal)$_3$Phen/LLDPE complex material. At the

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same time, the luminescence performance of the Eu,Pr(Sal)$_3$Phen/LLDPE has been researched.

Experimental

Reagents and materials

The reagents and raw processed materials used in this experiment are given in Table 1.

Preparation of the Eu(Sal)$_3$Phen and Pr(Sal)$_3$Phen

Eu(Sal)$_3$Phen was synthesized following the procedure developed by Yang [21]. The Eu(Sal)$_3$Phen was made from three raw materials: europium oxide (Eu_2O_3), salicylic acid (Sal), and 1,10-phenanthroline (Phen) at a molar ratio of 1:6:2. The procedure described below has been followed: 2.2 g of Eu_2O_3 was added into an aqueous 20 mL solution of HCl (10 mL H_2O and 10 mL HCl) and heated at 80–90 °C until complete dissolution. Continuous heating was required for converting Eu_2O_3–$EuCl_3$ and removing extra HCl and all water. Then the dried $EuCl_3$ had been dissolved by 100 mL anhydrous ethanol in conical flask at stirring, following the dropping of 50 mL of anhydrous ethanol 0.75 M solution of Sal. Then, we added 50 mL of anhydrous ethanol 0.25 M solution of Phen Drip Sal–ethanol solution and Phen–ethanol solution into $EuCl_3$–ethanol solution in a sequence and keep the obtained mixture heated at 50 °C and stirred at 600 r.p.m. for 6 h. Finally, the mixture was cooled down to room temperature. Adjust the pH value of the mixture to 6–7 by adding ammonia: water (1:1 volume ratio) and the product was obtained in a yellow precipitate form. The precipitate was kept overnight and then vacuum filtered and washed several times by anhydrous ethanol. The precipitate was first dried in oven at 80 °C for one day and then dried in vacuum oven until the weight remained constant. A yellow powder Eu(Sal)$_3$Phen complex is yielded. The Pr(Sal)$_3$Phen complex was prepared following the same procedure.

Preparation of Eu,Pr(Sal)$_3$Phen/LLDPE composites

Pr(Sal)$_3$Phen and Eu(Sal)$_3$Phen have been mixed according to different weight ratio. Following this, we blended the Eu,Pr(Sal)$_3$Phen mixture with LLDPE 7042 in a clean mixer (Haake, rheomix610, Ger.) during heating at 160 °C and stirring at 600 rpm 15 min later, the Eu,Pr(Sal)$_3$Phen/LLDPE composites have been prepared. The composites

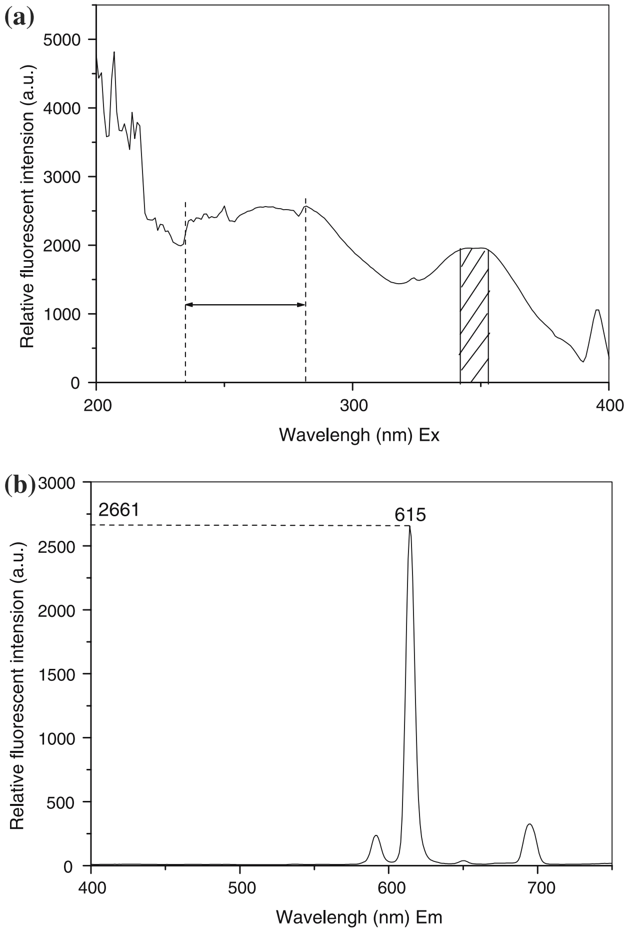

Fig. 1 The excitation spectra and emission spectra of Eu,Pr(Sal)$_3$Phen. (**a**) The excitation spectra of Eu,Pr(Sal)$_3$Phen (1:1) (Em = 615 nm); (**b**) The emission spectra of Eu,Pr(Sal)$_3$Phen (1:1) (Ex = 300 nm)

Table 1 Agents and raw processed materials

Reagents	Grades/TM	Abbreviation	Manufactures
Europium oxide	99.99%	Eu_2O_3	Shanghai Yuelong New Materials Co., Ltd.
Praseodymium oxide	99%	Pr_6O_{11}	Shanghai Yuelong New Materials Co., Ltd.
Salicylic acid	Analytical reagent	Sal	Beijing Yili Fine Chemicals Co., Ltd
1,10-phenanthroline	Analytical reagent	Phen	Beijing Xizhong Chemical Factory
Linear-low density polyethylenes	LLDPE-FB-18D022 DFDA 7042	LLDPE	Jilin Petrochemical filiale of china petroleum

have been patternmaking at 160 °C (>the melt-point of LLDPE) and at 250 kg pressure for 15 min. Subsequently, they have been cooled to room temperature with the same pressure for 10 min prior to any further experimentation.

Characterization and instrument

The fluorescent properties were examined by a Hitachi F-4500 fluorescence spectrometer under conditions of scanning rate: 2400 nm/min, scanning slit: 5.0 nm/5.0 nm ($\lambda_{ex}/\lambda_{em}$), and scanning photoelectric cell voltage: 400 V. The morphology of Eu,Pr$(Sal)_3$Phen particle was observed using a S-250-III scanning electron microscope (Cambridge Co). Crystal structures of the composites were examined on a D/MAX2500+PC Wide-angle X-ray diffractometer. In addition, Eu,Pr$(Sal)_3$Phen samples prepared by potassium bromide method were characterized by their IR absorptions with Hitachi 270-30 Fourier transform infrared (FTIR) spectrometer.

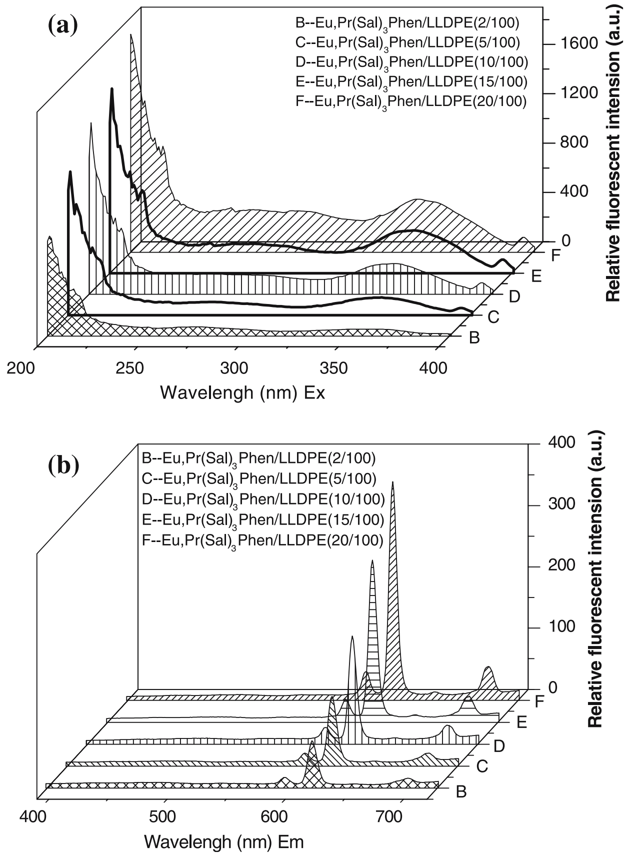

Fig. 2 The excitation spectra and emission spectra of the Eu,Pr$(Sal)_3$Phen(1:1)/LLDPE composites with different Eu,Pr$(Sal)_3$Phen(1:1) content. (**a**) The excitation spectra of the Eu,Pr$(Sal)_3$Phen(1:1)/LLDPE composites with different Eu,Pr$(Sal)_3$Phen(1:1) content; (**b**) The emission spectra of the Eu,Pr$(Sal)_3$Phen(1:1)/LLDPE composites with different Eu,Pr$(Sal)_3$Phen(1:1) content

Results and discussion

The fluorescent properties of Eu,Pr$(Sal)_3$Phen powder

The fluorescent properties of Eu,Pr$(Sal)_3$Phen powder have been analyzed as shown in Fig. 1a and b.

The Fig. 1a showed that the powder Eu,Pr$(Sal)_3$Phen could absorb UV of the 200–400 nm. The absorption band at the shaded area is due to the $\pi \rightarrow \pi*$ band of phen ligands. It indicates that the Eu,Pr$(Sal)_3$Phen complex cations exist [22]. The range of two dash lines in the Fig. 1a belongs to absorption Sal [23]. The emission spectra of Eu,Pr$(Sal)_3$Phen represented in Fig. 1b as can be seen, emit red–orange light at about 615 nm which belongs to the transition $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}. The red–orange light is characteristic emitted fluorescence of Eu^{3+} and beneficial for growth of crops. And the Pr^{3+} does not emit light at this excitation wavelength for Pr^{3+} and Sal do not have good matching.

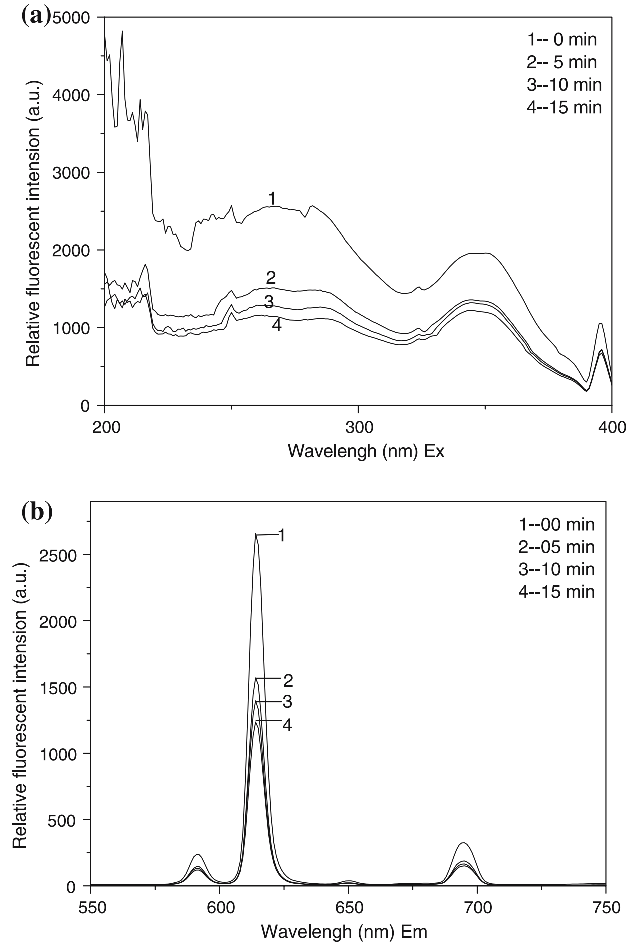

Fig. 3 The excitation spectra and emission spectra of the Eu,Pr$(Sal)_3$Phen treated for different time at 160 °C. (**a**) Excitation spectra of the Eu,Pr$(Sal)_3$Phen treated for different time at 160 °C; (**b**) Emission spectra of the Eu,Pr$(Sal)_3$Phen treated for different time at 160 °C

The fluorescent properties of Eu,Pr$(Sal)_3$Phen/LLDPE composites containing different contents of Eu,Pr$(Sal)_3$Phen

The Fig. 2a and b display fluorescent properties of Eu,Pr$(Sal)_3$Phen/LLDPE composites containing different contents of Eu,Pr$(Sal)_3$Phen (2, 5, 10, 15, and 20 phr. The phr is the content of Eu,Pr$(Sal)_3$Phen in 100 g LLDPE). Figure 2a is the excitation spectra (Em = 615 nm), and Fig. 2b is the emission spectra (Ex = 271 nm).

From Fig. 2, it is observed that the fluorescent intensity of the composites increases with the increase in the Eu,Pr$(Sal)_3$Phen (1:1) content in the matrix for both the excitation spectra and the emission spectra. And there is no fluorescent quenching happened even when the Eu,Pr$(Sal)_3$Phen (1:1) content reaches 20 phr in the matrix (the weight ratio of the Eu,Pr$(Sal)_3$Phen (1:1) is 16.7% in the composites). Figure 2a shows that the composites can absorb UV, which is harmful for the plant growth. It has been reported that there is increase in the decomposing speed of LLDPE is according to literatures [24, 25]. The syntheses composites in this work possess huge potential for practical applications of absorbing UV. Figure 2b shows that the composites can emit red–orange light region about 615 nm.

By comparing Fig. 1a with Fig. 2a and Fig. 1b with Fig. 2b, we know that the great change in luminescent intensity has been happened, which is caused by the concentration effect of Eu,Pr$(Sal)_3$Phen, on the other hand, probably by the result of machine rubbing Eu,Pr$(Sal)_3$Phen at high temperature 160 °C and high rate 100 rph.

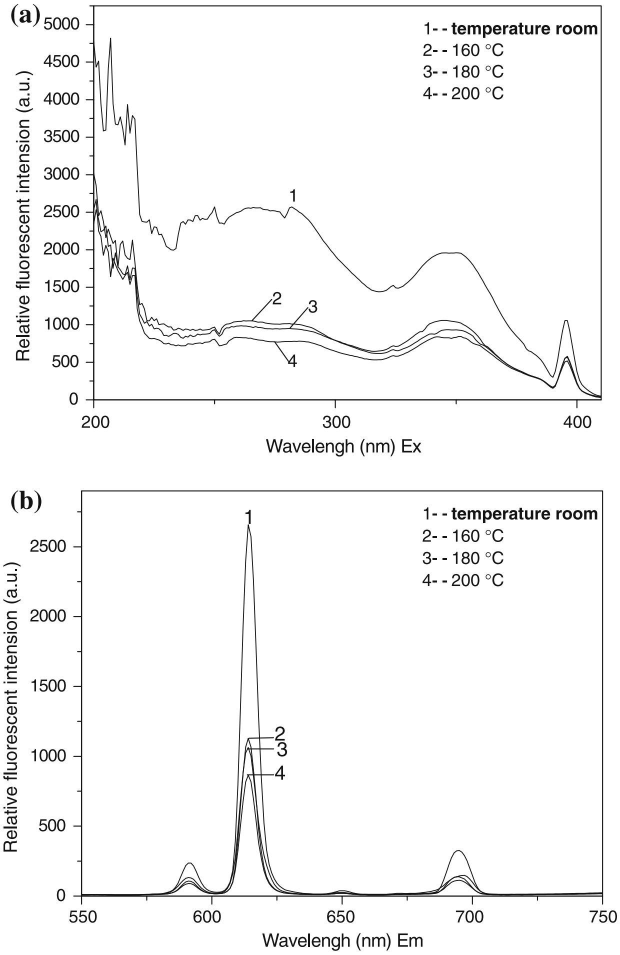

Fig. 4 The excitation spectra and emission spectra of Eu,Pr$(Sal)_3$ Phen treated for 10 min at different temperatures. (**a**) Excitation spectra of the Eu,Pr$(Sal)_3$Phen treated for 10 min at different temperatures; (**b**) Emission spectra of Eu,Pr$(Sal)_3$Phen treated for 10 min at different temperatures

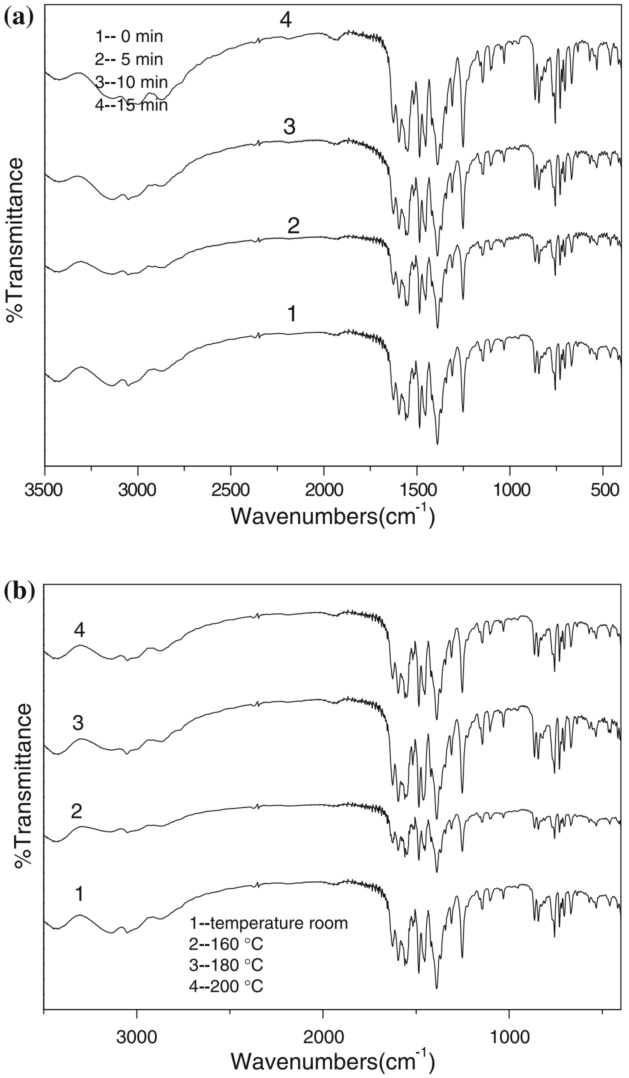

Fig. 5 The FTIR spectra of Eu,Pr$(Sal)_3$Phen treated for different time and at different temperatures. (**a**) The FTIR spectra of Eu,Pr$(Sal)_3$ Phen treated for different time at 160 °C; (**b**) the FTIR spectra of Eu,Pr$(Sal)_3$Phen treated for 10 min at different temperatures

The effects of preparation conditions on the fluorescent properties of Eu,Pr(Sal)$_3$Phen

Two sets of Eu,Pr(Sal)$_3$Phen(1:1)/LLDPE composites were prepared, which are heated at 160 °C during different periods of time (0, 5, 10, and 15 min) and at room temperature, 160, 180, and 200 °C during the same period of time (10 min). The effects of treated temperature and treated time on fluorescent properties have been researched. The Fig. 3a and b are fluorescent properties of Eu,Pr(Sal)$_3$Phen treated for different time at 160 °C.

The Fig. 3a and b showed that the fluorescent properties of Eu,Pr(Sal)$_3$Phen reduce with delay of treated time, not only in excitation spectra but also in emission spectra.

The Fig. 4a and b are fluorescent properties of Eu,Pr(Sal)$_3$Phen treated for 10 min at different temperatures.

The Fig. 4a and b displayed that the fluorescent properties of Eu,Pr(Sal)$_3$Phen reduce with increase in treated temperature.

To date, attempts have been made to understand the reasons that the fluorescent properties of Eu,Pr(Sal)$_3$Phen reduced with increase in treated temperature or time, the Eu,Pr(Sal)$_3$Phen formed were characterized by Fourier transform infrared (FTIR) spectroscopy and wide-angle X-ray diffraction (WAXD), as follows.

The chemistry structure of Eu,Pr(Sal)$_3$Phen was analyzed by FTIR. The Fig. 5a and b are FTIR spectra of Eu,Pr(Sal)$_3$Phen at different treated time and temperature, respectively.

The Fig. 5a and b confirmed that the station of characteristic peaks of Eu,Pr(Sal)$_3$Phen treated for different time and at different temperatures are the same. These indicated that the treated time and temperature did not affect chemistry structure of Eu,Pr(Sal)$_3$Phen.

Besides, the crystallization of Eu,Pr(Sal)$_3$Phen is reviewed and WAXD spectra of Eu,Pr(Sal)$_3$Phen are shown in Fig. 6a and b for the samples treated for different time at 160 °C and treated for 10 min at different temperatures, respectively. At the same time, the WAXD spectra of Sal and Phen were described in Fig. 6c and d.

From Fig. 6c it can be seen that the WAXD spectrum of Sal exhibited characteristic peaks at 11.04, 17.23, and 28.05° of 2*θ*, the Fig. 6d showed characteristic peaks of Phen at 2*θ* angles of 9.95, 17.21, 19.92, 22.37, and 30.11°. These peaks of Sal and Phen inexistenced in Fig. 6a and b. In addition, characteristic peaks of Eu,Pr(Sal)$_3$Phen appeared at 2*θ* angles of 7.85, 10.01, 12.30, and 32.55° in Fig. 6 a, b. At the same time, the Fig. 6a proved that the relative intensions of WAXD spectrum of Eu,Pr(Sal)$_3$Phen were unchanged at 2*θ* angles of 7.85°, 10.01°, and 12.30° during treated times changed, but the relative intension reduced when 2*θ* is 32.55. Otherwise, the Fig. 6b indicated that the relative intensions of WAXD spectrum of Eu,Pr(Sal)$_3$Phen were weakened when the treated

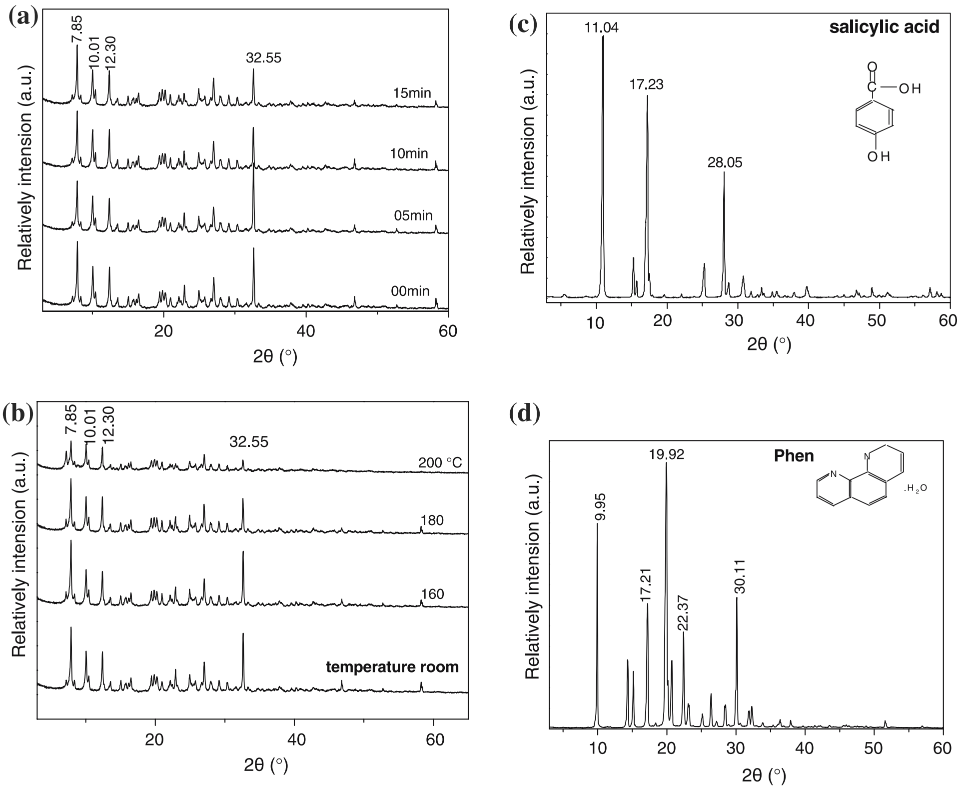

Fig. 6 The WAXD Spectra of Eu,Pr(Sal)$_3$Phen treated for different time (**a**) and at different temperatures (**b**), WAXD Spectra of Sal (**c**) and Phen (**d**). (**a**) The WAXD spectra of Eu,Pr(Sal)$_3$Phen treated for different time at 160 °C; (**b**) the WAXD spectra of Eu,Pr(Sal)$_3$Phen treated for 10 min at different temperatures; (**c**) the WAXD spectra of Sal; (**d**) the WAXD spectra of Phen

temperature increased at all of 2θ within same treated time, $2\theta = 32.55°$, especially.

Hereinbefore, this confirmed that the treated times and temperature affected crystal structure of Eu,Pr(Sal)$_3$Phen, ulteriorly affected luminescence performance of Eu,Pr(Sal)$_3$ Phen [21].

Track examination of luminescence performance of Eu,Pr(Sal)$_3$Phen/LLDPE composite materials placed into outdoor

The Eu,Pr(Sal)$_3$Phen/LLDPE composite materials were placed outdoor for 4 months and their luminescence performance is displayed in Fig. 7a and b.

Figure 7a and b showed that the luminescence performance of Eu,Pr(Sal)$_3$Phen/LLDPE composite materials had no evident change within 2 months. After 3 months, the luminescence performance was improved dramatically, yet after 4 months, it is clearly reduced. Considered, first (within 2 months), the luminescence performance, which of Eu,Pr(Sal)$_3$Phen in Eu,Pr(Sal)$_3$Phen/LLDPE composite materials, was reduced by light. And with the extend of time, Eu,Pr(Sal)$_3$Phen powder is dispersed in LLDPE matrix uniformly through "self-diffusion" and "self-dissolution" [26]. Thus, the luminescence performance enhanced because "fluorescence quenching" [27] has been reduced. And as time continues, dispersion of Eu,Pr(Sal)$_3$Phen powder in LLDPE matrix has been stabilized. The attenuation of Eu,Pr(Sal)$_3$Phen powder itself dominates. Meanwhile, the LLDPE matrix could not shelter Eu,Pr(Sal)$_3$Phen powder very well because aging resulted from weather effects. So the luminescence performance of Eu,Pr(Sal)$_3$Phen/LLDPE composite materials descends rapidly. In a word, light transformation function material—Eu,Pr(Sal)$_3$Phen/LLDPE composite material, which can be able to satisfy growth-need of crop during one quarter, has been prepared.

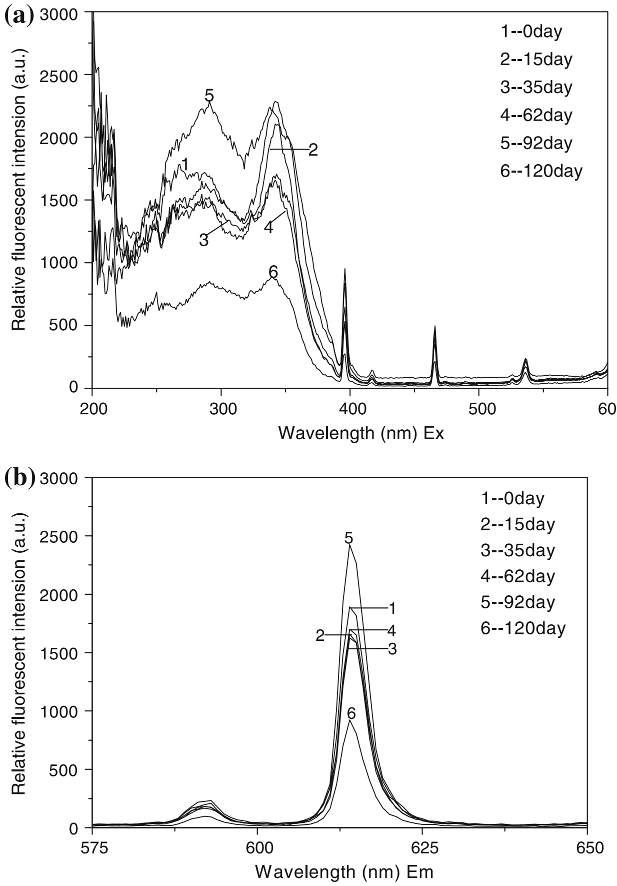

Fig. 7 The excitation spectra and emission spectra of Eu,Pr(Sal)$_3$ Phen/LLDPE (20/100) composite treated for different time at outdoors. (**a**) The excitation spectra of Eu,Pr(Sal)$_3$Phen/LLDPE (20/100) composite treated for different time at outdoors; (**b**) the emission spectra of Eu,Pr(Sal)$_3$Phen/LLDPE (20/100) composite treated for different time at outdoors

Conclusions

1. The luminescence intensities of Eu,Pr(Sal)$_3$Phen/LLDPE improve with the amount of Eu,Pr(Sal)$_3$Phen raising, and then drop down after reaching the maximal value at the loading of 20 phr (16.7% by weight) due to the appearance of "fluorescence quenching."
2. At the same treated temperature, longer the heat-treated time of Eu,Pr(Sal)$_3$Phen powder is, worse are the fluorescent properties; at the same treated time, higher the heat-treated temperature of Eu,Pr(Sal)$_3$ Phen powder is, worse are the fluorescent properties.
3. Light Transformation Function Material—Eu,Pr(Sal)$_3$Phen/LLDPE composites materials, which can be able to satisfy growth-need of crop during one quarter, has been prepared.

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